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Quantitative Palynofacies analysis as a new tool to study transfers of fossil organic matter in recent terrestrial environments.

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Abstract:

Classical palynofacies method, which consists of an organic concentrate microscopic qualitative observation after mineral phase dissolution, is commonly used in order to study sedimentary organic matter. In the present study we develop a new quantitative palynofacies method that allows organic particles mass concentrations to be determined in studied samples. This method was developed to help quantify the input of fossil organic matter (FOM) into modern environments as a result of sedimentary rocks weathering. Studied samples were collected from different pools, like bedrocks, weathering profiles, soils and riverine particles in an experimental watershed “Le Laval”. This watershed overlying Callovo - Oxfordian marls (1km² in area) is located

near Digne, Alpes-de-Haute-Provence, in France. In addition to palynofacies techniques, Rock-Eval 6 pyrolysis and Al_2O_3 content measurements (inductively coupled plasma emission spectrometry) were carried out on the samples. Obtained results show that this quantitative palynofacies method is suitable for FOM studies in modern environments, and FOM particles are quantified in the different pools. Results also give evidence that FOM alteration depends on the type of weathering, but also on the kind of organic particles. Soil formation under vegetation, resulting from the (bio)chemical weathering, lead to fossil organic particles concentration losses that do not exceed 30%. Elsewhere, mechanical weathering appears extremely fast and has no qualitative or quantitative influence on the observed FOM particles, which feeds directly into riverine stocks. FOM appears to be very resistant to weathering processes, this highlights its occurrence into supergene pools and then into carbon cycle. Quantitative palynofacies analysis is a new method adapted to such study, but can also be applied to other palynological, paleoenvironmental or archeological studies.

Keywords: Quantitative palynofacies, fossil organic matter, experimental watersheds, marls, carbon cycle, weathering processes.

1. Introduction

The study of the behavior of greenhouse gasses, such as CO_2 , requires an estimation of carbon fluxes which occur between different carbon pools such as the atmosphere, soil, biosphere and hydrosphere (Houghton, 1998; 2005; IPCC, 2007). Numerous estimates of river and soil carbon amounts have been calculated (Eswaran et al., 1993; Balesdent,

1996; Batjes, 1996; Adams and Faure, 1996; Carter et al., 1997; Holland, 1978; Degens et al., 1991; Probst, 1992; Amiotte-Suchet, 1995; Ludwig et al., 1996; Aitkenhead and McDowell, 2000), but all these estimates generally neglect Fossil Organic Carbon (FOC), originating from weathering and erosion of ancient and recent sediments. However at the global scale, shales and carbonates chemical weathering release between 0.04 and 0.09 Gt/yr of FOC (Di-Giovanni et al., 2002; Copard et al., 2007) and 0.04 to 0.08 Gt of FOC has been argued to be delivered to the world's oceans by rivers (Meybeck, 1993, 2005; Blair et al., 2003, 2004). These fluxes are the same order of magnitude as rivers global particular organic carbon load, estimated between 0.09 and 0.3 GtC/yr (Berner, 1992; Ludwig et al., 1996; Stallard, 1998), thus suggesting that FOC should be taken into account.

Numerous studies have already tracked FOC occurrence in different compartments, such as rivers (Kao et al., 1996; Di-Giovanni et al., 2000; Masiello and Druffel, 2001; Blair et al., 2003, 2004; Raymond and Bauer, 2001, 2004), soils (Lichtfouse et al., 1997a,b; Di-Giovanni et al., 1998a, 1999a,b, 2000; Copard et al., 2006) and recent sediments (Combaz et al., 1977; Tyson, 1995; Di-Giovanni et al., 1997, 1998b, 1999b, 2000; Eglinton, 1997; Leithold et al., 2001; Blair et al., 2003; Dickens, 2004a,b ; Wakeham et al., 2004) using a large analytical panel, such as microscopic (palynofacies method), isotopical (^{13}C , radiocarbon ages), geochemical (organic carbon, C, N), molecular and physical (IR spectra analysis) investigations. All these works reveal either -i) the discrimination of FOC from Recent Organic Carbon (ROC), or -ii) the quantification of FOC losses during rocks weathering and erosion, but neither can perform both operation simultaneously.

In this work, we propose a new quantitative optical method (quantitative palynofacies analysis) using a pollen standard and organic particles densities. This method allows the mass concentration of each type of organic particle in the studied samples to be obtained. Investigations were carried on marl weathering profiles because FOC content of such a sedimentary rock is higher than carbonate and sandstones, and these rocks represent about 30% of the global continental surface (Amiotte-Suchet et al., 2003).

2. Study area and sampling

The studied area is the “Le Laval” watershed located near Digne (Alpes-de-Haute-Provence, France, Fig. 1). The watershed is poorly vegetated (21% vegetation density) and the vegetation is mainly composed of grass, graminaceous plants, brooms, scots pines and oaks overlying Callovo-Oxfordian marly limestones (Mathys, 2006). Three weathering profiles were collected:

P1 (80cm thick) is a bedrock/weathered rocks (alterites) profile (Fig. 1) from a slope without vegetation context. 15 samples were collected every 5 cm, from the bedrock (>70 cm depth) to the surface.

P2 (140 cm thick) is a bedrock/alterites/soil profile (Fig. 1) from a wooded slope area. This profile consists of soil horizons (litter layers - OL, humic layers – OH, and organo-mineral layers -A) in the first 20 cm, followed by 105 cm of alterites and then by bedrock. Two types of material were distinguished: -i) compact fragments of rock (PL)

and -ii) fine and friable elements (TF). 47 samples were collected every 5 cm (3 soils layers, 22 PL samples and 22 TF samples).

P3 (60 cm thick) is an alterites/soil profile (Fig. 1) from a flat pasture area. The profile is composed mainly of clay in the first 30 cm, and then of a mixture of clay and rock fragments. 10 samples were collected every 6 cm.

Riverine particle samples were also examined. Height Laval suspended load (SL) samples were collected using automatic sampling between July 2006 and January 2008 and two bed load (BL) samples were collected in 2002 and 2006.

3. Methods

3.1. Microscopic investigations

Optical investigations (palynofacies method) were performed with a DMR XP Leica microscope by using the transmitted light mode. Initially developed by Combaz (1964), the palynofacies method consists of a study of thin slides of a total assemblage of particulate organic matter isolated from sedimentary rocks using HCl–HF. The approach involves the distinction of different categories of petrographic components based on their size, form and colour, and an estimate of their relative proportions in the particular organic assemblage (Combaz, 1980; Tyson, 1995). Relative quantification was performed with a 50 x objective and it is effective when 500 particles are counted,

because variations of relative abundances were also lower than 5% (Sebag et al, 2006a,b).

Quantitative methods have already been developed by different authors (Battarbee and Kneen, 1982; Vernal, 1987) in order to evaluate diatoms, pollens, or microfossil abundance in sediments. In these studies, a known number of standard particles (*Lycopodium* or *Eucalyptus* pollens, polystyrene microspheres) is incorporated in the studied samples. After counting, the surface relationship between standards and studied particles allows to estimate particles occurrences (i.e. number of particles).

Here, quantitative palynofacies analysis is based on the incorporation of a known mass of standard (*Cupressus* pollen) in organic concentrate after acid attacks. *Cupressus* pollen was chosen as a standard because of its strong reaction under UV excitation that helps greatly in its identification (Fig. 2d). For each sample, the mass concentration of each kind of particle in organic concentrate is obtained after observations and counting (500 particles) as follow (eq.1):

$$\text{eq.1) Particles (mg) in organic concentrate} = \frac{\text{Mass standard added (mg)} \times \text{Particles area (\%)}}{\text{Standard area (\%)}} \times \frac{\text{Particles density}}{\text{Standard density}}$$

This corresponds to a comparison between the mass of standard added to the area ratio between the studied organic particle and standard which are then corrected by the organic particles densities.

Particles mass concentrations in initial sample (prior acid attacks) are calculated as follow (eq.2):

$$\text{eq.2) Particles mass concentration (mg/g sample)} = \frac{\text{Particles (mg)}}{\text{Initial sample mass (mg)}}$$

3.2. *Rock-Eval pyrolysis*

The geochemical characteristics of the samples were acquired using Rock-Eval 6 pyrolysis (RE6, Vinci Technologies®). Previously developed for petroleum purposes and the analysis of sedimentary rocks, the method has been now been successfully tested for recent material (Di-Giovanni et al., 1998; Disnar et al., 2003; Copard et al., 2006; Sebag et al., 2006c).

The protocol consists of two successive stages performed under a temperature program of 30 °C min⁻¹. The first consists of pyrolysis of 100 mg of crushed sample in an oven. Hydrocarbon and oxygenated products released during a temperature increase from 200 to 650 °C are removed via a N₂ flow and quantified with flame ionization and infrared detectors. The second stage consists of oxidation in an oven of the carbonaceous residue subjected to a temperature increase from 400 to 750°C (Espitalié et al., 1985; Lafargue et al., 1998; Behar et al., 2001).

Analysis of the pyrolysis signal provides a number of parameters, such as -i) T_{max}, the temperature in °C at which the maximal hydrocarbon (HC) release occurs, and -ii) the hydrogen index (HI, in mg HC g⁻¹ TOC), which can be defined as an indicator of the hydrogen richness of a sample. The organic carbon content (OC) is given by the total

organic carbon (TOC, expressed in wt %), that is equal to the sum of pyrolysed OC and residual OC provided by the oxidation stage.

3.3. Al₂O₃ contents

Quantitative palynofacies aims to quantify FOM mass concentrations in studied samples, but it also aims to estimate FOM loss during bedrock weathering. Indeed, mineral fractions can undergo significant changes in chemical composition during weathering processes (i.e. carbonate dissolution, silicates hydrolysis). Thus, an equivalent FOM mass concentration into two compartments (i.e. soil and bedrock) can be interpreted in two ways: -i) a FOM loss during bedrocks weathering or -ii) an evolution of FOM concentration caused by a loss of mineral phase. To overcome this problem, all mass concentrations were normalized to the Al₂O₃ contents of studied samples as this oxide is resistant toward chemical dissolution. (Campy and Macaire, 1989, 2003).

Al₂O₃ contents were obtained by ICP analysis (inductively coupled plasma emission spectrometry) with a Jobin-Yvon ULTIMA[®] spectrometer. 100 mg of finely crushed raw sample (prior to acid attacks) is mixed with 250 mg LiBO₂ and melted at 1000 °C for 5 min under argon. The pearl produced is then dissolved in nitric acid and the solution is then pulverized in an argon plasma (10 000 K). This leads to -i) the dissociation of matter into atoms and ions and -ii) the emission of characteristic wavelengths when atoms return to a lower energy states.

4. Results

4.1. Quantitative palynofacies investigations

4.1.1. Particles description

Twelve categories of organic particles were identified in the samples following different morphological and textural criteria (palynofacies observations in transmitted and reflected light, Fig. 2). Because the present study deals with the measurement of the density of each of categories of organics particles, we firstly present all particles in detail. For the sake of brevity, only major classes were described in the following sections.

- **Amorphous particles (Fig. 2a):** 1) clear and granular amorphous organic matter (CGAOM) consists of group of colloidal particles that appear gray or yellow when under transmitted light, and opaque or with a slight orange tint under reflected light. Their dimensions are highly variable between 10 μm and 100 μm , 2) reddish amorphous organic matter (RAOM) consists of groups of colloidal particles that appear dark red under transmitted light and with a black matrix appearance under reflected light. This class is associated with mineral matter and frequently with pyrite. These particles are generally small in sizes and ranged between 10 and 100 μm , 3) gelified amorphous organic matter (GA) have no internal structure and have an orange-red colour under transmitted and reflected light. These particles can reach a very large size over than several hundred μm .

- **Ligno-cellulosic fragments (Fig. 2b):** 4) dark degraded ligno-cellulosic fragments (DDLFC) show visible internal structures inherited from the original organic material.

These particles have a dark brown colour under transmitted light due to an advanced pedological evolution (degradation and/or oxidation) and they appear dark under reflected light, 5) translucent ligno-cellulosic fragments (TLC) show visible internal structures. These particles are generally translucent under transmitted light and black under reflected light, 6) gelified ligno-cellulosic fragments (GLC) show traces of internal structures but suffer of a higher state of gelification. They correspond to a more advanced degradation stage giving them a reddish-orange colour under transmitted and reflected light, 7) opaque ligno-cellulosic fragments (OLC) do not display any identifiable structure and show high reflectance under reflected light observation. These particles are subdivided according to their shapes (elongated - el OLC, squat - sq OLC, complex - c OLC, concave - conc OLC); we have also distinguished the corroded outline opaque ligno-cellulosic fragments (CoOLC) showing a very high and "metallic" reflectance.

Ligno-cellulosic fragments dimensions are highly variable between 10 and 100 μm .

- **Gelified debris (Fig. 2c):** These particles have homogeneous contours and textures and exhibit high reflectance. We distinguish 8) gelified debris (GD) that are fully transparent under transmitted light and 9) opaque gelified debris (OGD) which internal surfaces appear dark under transmitted light. These particles are generally small and rarely exceed 10 μm .

- Other organic particles (Fig. 2d) easily recognisable due to their specific morphology were also observed as: 10) mycelium fragments (Myc) which are elongated and have a colour tint ranging from light brown to brown under transmitted light. Size of these particles exceed several hundred μm , 11) cuticular fragments (Cut) corresponding to some residues of the outer membranes of higher plants. Their size are very variable and

can exceed several hundred μm , 12), spores and pollen grains (SP) which are the reproductive cells of macroflora. These particles are generally small and reach only 10 μm .

We also report a relative proportion of framboidal pyrite (resistant to acid treatment).

4.1.2. Particle density

The particle densities were measured using various density liquids (ethanol – 0.8 g/cm^3 , water -1 g/cm^3 and bromoforme – 2.9 g/cm^3) which mixing provided various densities solutions (0.8, 1, 1.3, 1.5, 1.7 and 1.9 g/cm^3). Two samples were examined: a bedrock organic concentrate located at the bottom of the P2 profile and an OH layer located at the top of the same profile. Both samples were selected because their organic content covers all particles observed in this work, as indicated by microscopy observations. For each density fraction, we estimate the carbon recovered using Rock-Eval pyrolysis TOC (%) as follow (eq.3):

$$\text{eq.3) Carbon mass recovered in the fraction (mg)} = \\ \text{fraction weight (mg)} \times \text{fraction TOC (\%)}$$

After palynofacies counting, we estimate the carbon mass for each organic particle in a fraction using the following equation (eq.4):

$$\text{eq.4) Particles organic carbon in a fraction (mg)} = \\ \text{carbon mass recovered in the fraction (mg)} \times \text{particle area in the fraction (surfaces counting - \%)}$$

Obtained results for OH and PL samples organic particles are expressed in Fig. 3.

OH sample (Fig. 3a) mainly contains ligno-cellulosic fragments, GA, Cut and Myc particles. RAOM, OLC, GD and pyrite particles are very rare or absent. The characteristics of the individual organic particle groups are given below:

OH sample amorphous particles: CGAOM mostly occurs in the less dense fractions and maximum Corg is recovered at a density of 1 g/cm³ (15.75 mg); GA particles have a more complex distribution with two maximum, between 0.8 and 1 g/cm³ (59.6 mg) and between 1.3 and 1.5 g/cm³ (102.4 mg).

- **OH sample ligno-cellulosic fragments:** DDLC particles are mostly collected between 1.3 and 1.5 g/cm³ (15.3 mg), whereas TLC and GLC are between 0.8 and 1 g/cm³ (respectively 37.3, 103.4 mg).

Myc and Cut particles are mostly represented between densities of 0.8 and 1 g/cm³. SP particles can be found in a wide range of densities, from 0.8 to 1.5 g/cm³.

PL samples (Fig. 3b) mainly consist of OLC, GD and ROAM particles. These particles appear to be denser than those of the OH sample and none remains in suspension at the density of 1.

- **PL sample amorphous particles:** ROAM are mostly collected in the two fractions equal or below 1.3 g/cm³ (8.3 and 10.7 mg) and in suspension at a density of 1.5 g/cm³ (21.2mg).

- **PL sample opaque ligno-cellulosic fragments:** el OLC occur between 1.3 and 1.5 g/cm³ (2.4 mg); c OLC are found between 1.7 and 1.9 g/cm³ (1.96 mg) and conc OLC are observed in all fractions, with a slight predominance between 1.5 and 1.7 g/cm³ (1.1 mg) and between 1.7 and 1.9 g/cm³ (0.8mg); Co-OLC particles are present in the

densest fractions above 1.7 g/cm³ (1.5 mg) and above 1.9 g/cm³ (1.4mg); sq OLC seem to be found preferentially in more than one density fraction, below 1.3 g/cm³ (4.9 mg) and between 1.5 and 1.7 g/cm³ (11 mg).

- **PL sample gelified debris:** GD particles are poorly present and are collected in all fractions between 1 and 1.5 g/cm³ with a slightly predominance in fraction equal or below 1.3 g/cm³ (0.47 and 0.6 mg); OGD mostly present in fraction equal or below 1.3 (9 and 13.8 mg).

- PL sample pyrite is too dense to be found in these fractions and is poorly collected in studied samples.

All these results allow us to assign an approximate density for each kind of particle (Table 1).

4.1.3. Quantification of samples organic particles

Particles were grouped according to their optical properties: all OLC, all other ligno-cellulosic fragments (as LC), GD with OGD (as GDgr), and Myc, Cut and SP as divers (Div).

In the P1 weathering profile, organic content (Fig. 4) is homogeneous and the samples reveal a strong predominance of OLC (between 0.176 and 0.296 mg/g), RAOM (between 0.109 and 0.192 mg/g) and GDgr (0.061 and 0.113 mg/g). In contrast, pyrite particle concentrations show significant changes along the profile and their proportions decrease from bottom to surface (from 0.268 to 0.034 mg/g).

P2 weathering profile:

For soil samples, quantitative palynofacies analysis has not been applied to samples OL and OH because standard particles are very small (20 μm) comparatively to large and slightly altered recent organic particles observed in these samples (up to 1 mm). This difference makes the observation of standard particles difficult and classical (qualitative) palynofacies is here used (Fig. 5a). OL and OH samples mainly contain LC particles (> 47 %) and in less proportion CGAOM, GA and Div particles. Other organic particles and pyrite are absent or occur in very small quantities. A layer sample exhibits more variable organic content (Fig. 5b) and contains OLC (0.163 mg/g), RAOM (0.132 mg/g), GDgr (0.070 mg/g), LC (0.543 mg/g) and GA (0.664 mg/g) particles. Pyrite is absent from this sample.

PL samples organic content (Fig. 5b) is similar to that observed in profile P1. Maximum concentrations are obtained between 110 and 125 cm depth (OLC, RAOM and GDgr concentrations can reach 0.512, 0.317 and 0.248 mg/g). Pyrite is observed in overall samples, and instead a great variability, a decrease of obtained values from bottom to surface is observed, with concentration dropping by about 0.219 to about 0.015 mg/g.

TF samples exhibit an intermediate organic content between PL and A layer samples (Fig. 5c). OLC, GDgr and RAOM concentrations are the same order as in PL samples, with a maximum between 110 and 125 cm depth (OLC, RAOM and GDgr concentrations can reach 0.500, 0.314 and 0.184 mg/g). Samples collected between 20 and 40 cm depth are generally poor in these particles with average concentrations of 0.192 mg/g for OLC, 0.134 mg/g for ROAM and 0.55 mg/g for GDgr. Pyrite is either completely absent or present in very small quantities in TF samples. Other particles concentrations decrease according with depth from 0.5 to 0.01 mg/g for LC and from

0.422 to about 0.18 mg/g for GA. CGAOM and Div are poorly present and their concentrations decrease with the depth as well.

P3 weathering profile:

Organic contents are similar to that observed in P2 profile A layer and TF samples (Fig. 5d). OLC, RAOM and GDgr amounts are quite constant, while others particles concentrations decrease with depth (i.e. from 1.415 to 0.018 mg/g for LC, from 0.531 to 0.021 mg/g for GA, from 0.122 to 0.007 mg/g for Div and from 0.167 to 0.005 mg/g for CGAOM). Pyrite is absent or is slightly present (< 0.013 mg/g).

Riverine particles:

“Le Laval” SL and BL samples organic content (Fig. 5e) mainly consists of OLC (between 0.221 and 0.403 mg/g), RAOM (between 0.195 and 0.297 mg/g), GDgr (between 0.042 and 0.070 mg/g) and pyrite (between 0.033 and 0.328 mg/g). LC, GA, Div and CGAOM are slightly present and the sum of these particles does not exceed 0.125 mg/g.

4.2. Chemical investigations

4.2.1. Rock-Eval analysis

P1 weathering profile: samples (Fig. 6) are homogeneous and exhibit low TOC values (between 0.3 and 0.52 %), low HI values (between 11 and 22 mg HC g⁻¹ TOC) and Tmax values close to 520°C.

P2 weathering profile:

- Soils samples: OL and OH litters samples (Fig. 7a) are characterized by high TOC values (40.67 and 25.55 %), high HI values (446 and 309 mg HC g⁻¹ TOC) and low Tmax values (336 and 330°C). A layer sample exhibits different TOC, HI and Tmax values (respectively 1.46 %; 164 mg HC g⁻¹ TOC and 410°C). PL samples (Fig. 7a) show very similar TOC, HI and Tmax values to those observed in profile P1, except for the samples collected between 110 and 125 cm depth, which have more important TOC (between 0.62 and 0.69 %). TF samples (Fig. 7b) exhibit more contrasted values. TOC and HI values decrease with depth (1.13 to 0.49 % and 128 to 14 mg HC g⁻¹ TOC) whereas Tmax increases in the deepest samples (from 400 to 520°C).

P3 weathering profile: P3 profile (Fig. 7c) samples TOC values decrease with depth before stabilizing at 36 cm (from 1.73 to approximately 0.3 %), HI values also decrease with depth (from 180 to 63 mg HC g⁻¹ TOC) and Tmax values are close to 400 °C .

Riverine particles: Riverine particles (Fig. 8) present similar values to those obtained in PL samples. Independently of the sampling period, SL and BL samples exhibit low TOC values (between 0.48 and 0.62 %), low HI values (between 11 and 29 mg HC g⁻¹ TOC) and some Tmax values close to 520°C (except 2006 BL samples, which exhibit a higher Tmax of 575 °C).

4.2.2. Al_2O_3 contents (Fig. 9)

For P1 profile, Al_2O_3 contents decrease with depth from 15.5 to 12.5 %. PL samples of P2 profile exhibit some Al_2O_3 contents ranging between 14 and 17.52 %, while TF

samples contain few Al_2O_3 (13.06-16.2 %). This low content is also observed in P3 samples, where values are ranged between 13.00 and 14.95 %.

Al_2O_3 contents in riverine particles are similar to those measured in weathering profiles with an average of 14.9 %.

5. Discussion

5.1. Identification of fossil organic matter and recent organic matter

Bedrocks samples show a palynofacies mainly dominated by OLC, ROAM and GDgr that can altogether represent 95 % of the organic matter. These particles are not found in the OL sample, which is mainly dominated by LC, GA, Div and CGAOM. With these results, we are able to discriminate and follow recent and fossil organic matter all along the studied profiles.

5.2. Method validity

Quantitative palynofacies method would give the opportunity to assess organic matter mass percentage (OM wt%). To test its validity, results were compared with TOC % obtained by Rock-Eval analysis (TOC % = OC wt%).

Case of fossil organic matter (FOM): For P1 and P2 profiles, bedrocks and PL samples mainly contain FOM. For these samples, we obtain an organic matter/organic carbon ratio (OM wt%/TOC %, i.e. quantitative palynofacies/RE6 pyrolysis) of 1.31 ± 0.25 ;

which is consistent with some values found in literature for mature organic matter (Trichet., 2006).

Case of recent organic matter (ROM): The estimation of palynofacies accuracy to quantify ROM is more difficult, since the OM/OC ratio can evolve during soil processes (Disnar et al., 2003). OC content (OC wt%) was therefore assessed by using: -i) the FOM and ROM wt% obtained by quantitative palynofacies, -ii) the OM/OC ratio of 1.31 previously get for FOM (i.e. OLC, ROAM and GDgr particles) and -iii) the OM/OC ratio of 1.7 for ROM (LC, GA, Div and CGAOM particles) given by literature (Duchaufour, 2001). Calculation of OC (wt%) is given as follow (eq.5):

$$\text{eq.5) Sample OC (wt\%)} = \frac{[\text{FOM OC (wt \%)}]}{1.31} + \frac{[\text{ROM OC (wt \%)}]}{1.70}$$

A difference of $\pm 15.5 \%$ (Fig. 10) is observed between TOC (%) given by RE6 pyrolysis and this calculated OC content. In detail, for samples showing high TOC values ($> 0.9 \%$) this new method systematically provides lower OC (wt%). Several reasons can explain this trend. First, optical observations on samples having a high TOC values (i.e. ROM in organic horizons) reveal a significant proportion of large ROM organic particles as gelified amorphous organic matter (AG). Consequently, the standard surface (pollens) used seems to be insufficient to quantify these particles. Second, ROM contains more acido-soluble compounds, notably in litter where there is highest TOC values, which are lost during preparation (20 to 30 % of ROM).

Quantitative palynofacies allows to quantify observed fossil organic particles in different samples, with an error of $\pm 15\%$. ROM quantification is more delicate as this

method systematically underestimates its contribution. However, this is not a real problem for our study, which focuses on FOM, but this highlights that the quantitative palynofacies method must be improved for other studies, focusing on ROM. Indeed, another larger standard should be used to quantify larger organic particles.

5.3. FOM evolution during rocks weathering

Quantitative palynofacies results were normalized with Al_2O_3 contents. These reports are noted AR (aluminium ratio).

Bedrocks /weathering profiles transition: Alterites formations are mostly dominated by bedrocks chemical weathering (Campy and Macaire, 1989, 2003). This transition would have a low influence on FOM quantity and quality. FOM AR values vary between 0.28 and 0.38 in P1 profile; and between 0.27 and 0.59 in P2 PL profile (Fig. 11a,b). There are also any trends in AR values whatever the diverse observed FOM previously seen (cf. section 4.1.3.). Conversely, along these two profiles a significant decrease in pyrite content is observed as illustrated by AR values that drop from 0.017 to 0.003 in P1 profile and from 0.016 to 0.001 in P2 PL profile (Fig. 12). This strong sensitivity of pyrite to weathering processes was already evidenced in previous study (Petsch et al., 2000).

Weathering profiles/Soils transition: Soil formation is mainly controlled by (bio) chemical weathering (hydrolysis, oxidation due to water infiltration and biological activity). In A soil layer from P2 profile, organic matter is a mixing of FOM and ROM

(principally GA) (Fig. 11b). The transfer between weathering profiles is accompanied by a decrease in FOM concentration as testified by a drop in the FOM AR value from 0.038 in PL samples (average) to 0.022. There is no change in FOM evolution along P3 profile (Fig. 11c). Indeed, OLC, RAOM and GDgr AR values remain relatively constant from the bottom to the top of the profile (respectively around 0.011, 0.006 and 0.008). Conversely, a rapid ROM decrease is however observed with depth (ROM AR falls from 0.161 to 0.004).

Weathering profiles / TF transition: In P2 profile, organic matter from TF samples is composed of FOM and ROM (mainly GA and GLC) (figure10b). ROM occurrence quickly declines with depth. FOM appears to be more resistant and shows, from 40 cm depth to the bottom of the profile, a concentration close to that estimated in PL samples (FOM AR value average 0.04). OLC particles are slightly more concentrated in TF samples as well as RAOM particles while GDgr particles are slightly less concentrated (Fig. 11b). This shows that chemical weathering does not affect FOM, except for GDgr particles. 20 to 40 cm depth range differs because FOM concentration in the TF samples is close to those measured in the P2 A layer sample. FOM losses are close to 28 % between PL and TF samples (Fig. 11b), but such losses vary according to the nature of the observed particles. Indeed, OLC particles resist to weathering, while ROAM and GDgr particles are more sensitive. In fact their losses reach 39 and 43 % (Fig. 11b). We also note that pyrite disappears in TF samples (Fig. 12).

Bedrocks / riverine particles transition: Riverine particles are directly produced by a direct mechanical erosion of the marls by water streaming (Di Giovanni et al., 2000).

This would have no impact on FOM concentrations. Indeed obtained results indicate that bedrock to riverine particles transfer (Fig. 11d) does not have significant quantitative and qualitative impacts on liberated FOM. In addition, pyrite is found in all riverine particles samples (Fig. 12) suggesting an absence of weathering during this transfer.

5.4. FOM occurrence in modern pools

Our results show that FOM can occur in significant quantities in modern C pools. For the studied watershed, FOM can contribute for about 98% of total organic matter in PL samples, 85 % in riverine particles and between 20 and 90 % in TF and A layer samples. Obtained results pointed out that FOM and pyrite are found at the watershed outlet without qualitative or quantitative changes. Considering that the time transport of fluvial particles between “le Laval” watershed and Rhône delta does not exceed five days (IRS, 2001), our results suggest that FOM could significantly contribute to Rhône organic content. To extend our results, this means that FOM contribution has to be definitively taken into account in riverine loads and in soils carbon contents at local, regional and global scales.

5.5. Factors controlling FOM alteration

It appears that FOM alteration depends on the weathering type, but also on the kind of particles.

Bacterial activity mainly occurs in wooded areas (weathering profiles/soils and PL/TF transitions) and associated FOM losses reach only 30%. OLC particles are more resistant whereas RAOM and GDgr losses reach an average of 40 %. Conversely, pyrite is very sensitive and its loss attains 90 % (Fig 12). These results are in agreement with some previous studies; indeed Petsch et al (2000) showed a FOM partial mineralization along weathering profiles, whereas Copard et al (2006) showed that weathering process does not affect all FOM compounds in the same way.

Chemical weathering is mainly observed at the profiles bases (bedrocks / alterites) and seems to have no impact on marls organic content, only pyrite particles are affected.

Mechanical weathering (bedrocks/riverine particles transition) has no impact on marls organic contents. Pyrite particles occurrence in riverine particles despite its sensitivity to weathering can be explain by the geomorphological context. Indeed, Callovo-Oxfordian marly limestones are characterized by a very strong erosion rate and by typical badlands morphology with V-shapes gullies (Mathys, 2006). Because of its intensity, mechanical weathering seems to be the main factor limiting (bio)chemical weathering, but as consequences, promotes FOM and pyrite export.

5.6. Callovo-Oxfordian marly limestones FOM representativeness

According to RE6 values as $T_{max} > 500^{\circ}\text{C}$, very low HI (generally $< 30 \text{ mg HC g}^{-1} \text{ TOC}$), FOM in Callovo-Oxfordian marly limestones is thermally mature. This may explain the low sensitivity of this OM to weathering. However, our results can only be extrapolated to FOM which present some similar features as: -i) the same physical and chemical properties (i.e. the same OM precursor), -ii) the same environmental deposit

(i.e. the same early diagenetic conditions and mineral protection), -iii) the same geological history (i.e. the same maximum temperature of burial recorded by FOM leading to a specific maturity degree) and -iv) the same geomorphological context (i.e. the same weathering context depending on climate and geology).

Indeed, all these previous points have impacts on the sensitivity of FOM toward weathering processes and erosion. For examples, Petsch et al., (2000) showed that FOM contained in organic carbon rich bedrocks (black shales) is very sensitive and losses recorded can reach 60 to 100 % along weathering profiles. Conversely, Fredericks et al. (1983) showed that some mature bituminous coals are more resistant and C-losses reach only 20 % in the same context.

Conclusions

Quantitative palynofacies is a new and promising method that enables both taking into account organic matter diversity and quantifying its contribution in studied samples with a sensitivity close to (± 15 %). This method allowed us: -i) to discriminate ROM from FOM particles, -ii) to quantitatively follow FOM during and after its releasing; and -iii) to highlight FOM resistance to weathering process (observed losses do not exceed 30 %).

In detail, transfers between compartments are accompanied by some losses in FOM particles. These ones depend on the organic constituent's nature, but also on the kind of transfer. A gradient of lability can be built from OLC (most resistant) to GDgr (most labile) particles. We also observe different trends in the FOM behavior during the different transfers occurring in continental surfaces. Thus, bedrocks/riverine particles

and bedrocks/alterites transfers have not impacts on FOM; while weathering profiles/TFand weathering profiles / soils transfers imply the maximum FOM losses (30 %).

Such results underline that FOM delivery in continental surfaces by weathering can not simply act as a source of carbon to the atmosphere or a direct input in supergene C reservoirs. Indeed FOM fate appears to be mainly controlled by the nature of weathering processes (i.e. hydrolysis, bacterial activities) and further studies should be performed to clarify the FOC role in the carbon cycle in terms of delivery and fate. Fossil contribution should then be taken into account in organic stocks and fluxes estimates both at local than at global scales.

Finally, this method has a wide range of applications. For example, quantitative palynofacies could be used for paleoenvironmental reconstructions as it enables to track and quantify different organic markers in various compartments (soils, marine or lacustrine sediments).

Acknowledgements

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Figure captions

Fig. 1. Geographical location of “le Laval” watershed and schematic weathering profiles studied. *Compact fragments of rock samples (PL); fine and friable elements samples (TF); suspended load samples (SL); bed load samples (BL); litter layers samples (OL); humic layers samples (OH) and organo-mineral layers samples (A).*

Figure 1

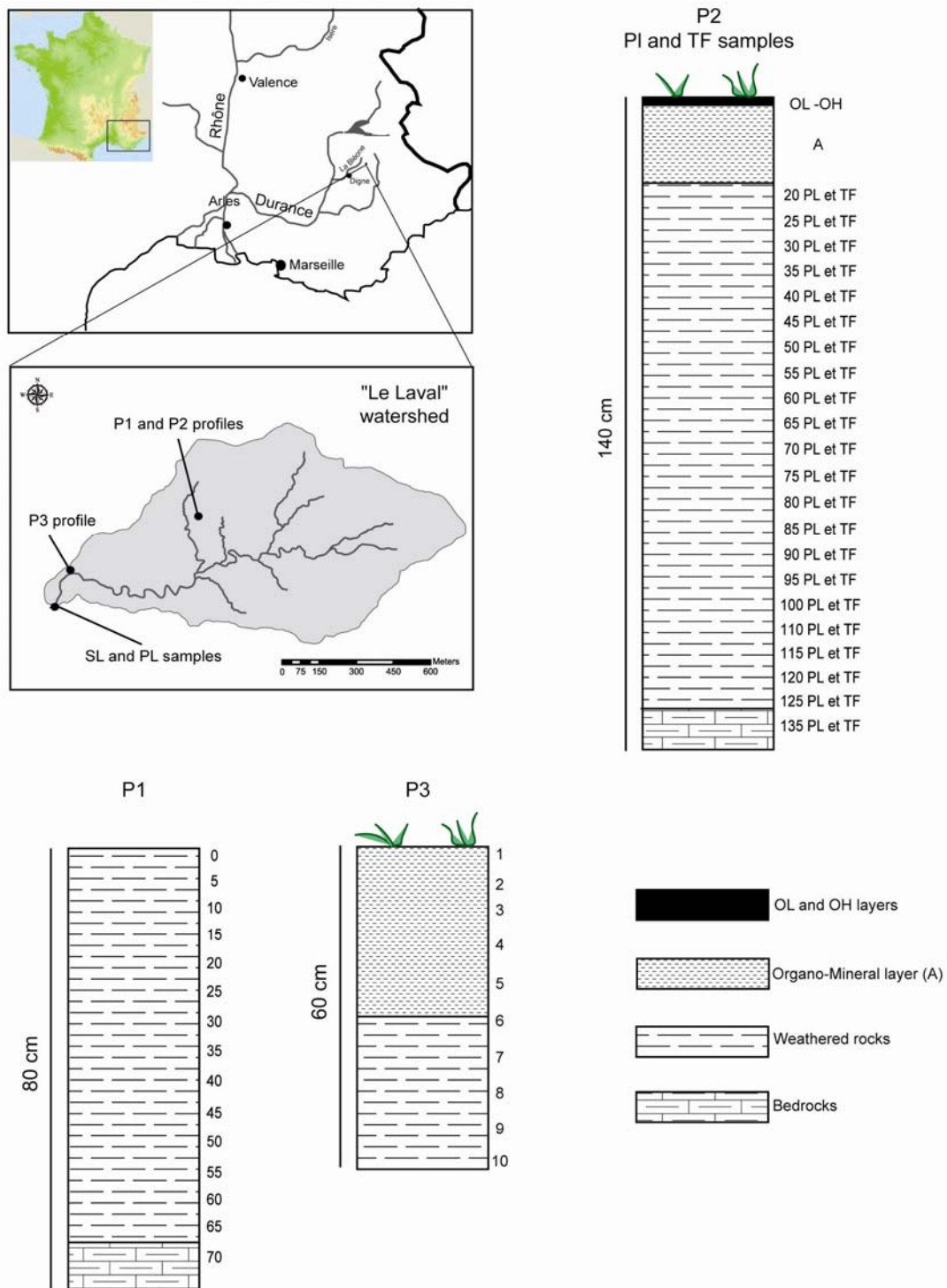
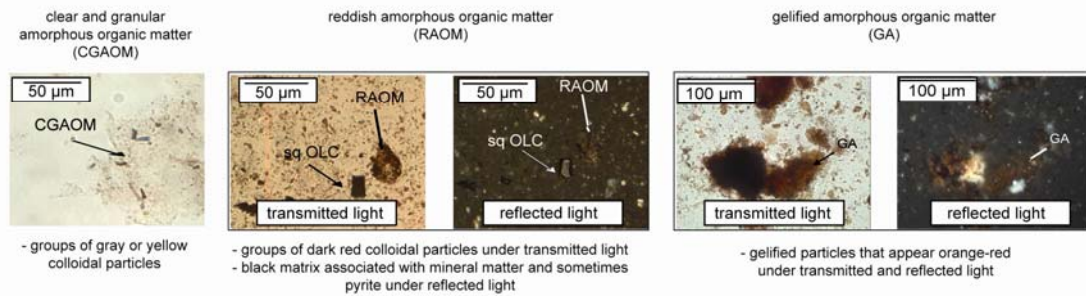


Fig. 2. Categories of particulate organic matter distinguished from morphological criteria : clear and granular amorphous organic matter (CGAOM), - reddish amorphous

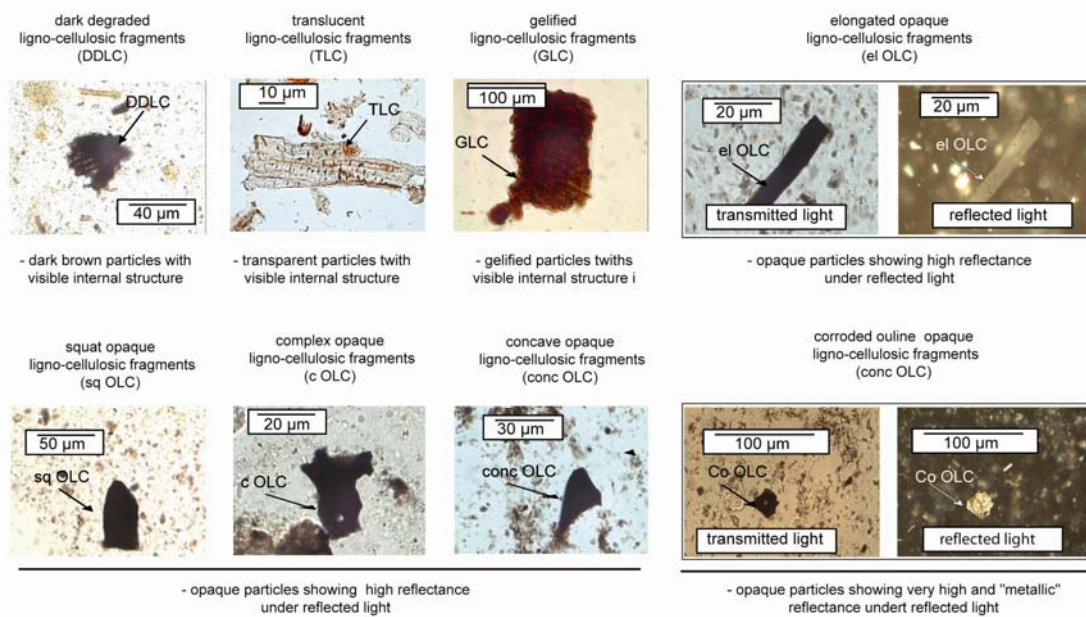
organic matter (RAOM), - gelified amorphous organic matter (GA), - gelified debris (GD), - dark gelified debris (OGD), opaque ligno-cellulosic fragments (OLC) fragments that do not display any identifiable structure as well as any fluorescence under UV excitation. These particles are separated by their shapes (elongated - el OLC, squat - sq OLC, complex - c OLC, concave conc OLC), - corroded outline opaque ligno-cellulosic fragments (CoOLC), - cuticular fragments (Cut),- spore and pollens (SP), - dark degraded ligno-cellulosic fragments (DDLCL) ; - translucent ligno-cellulosic fragments (TLC),- mycelium fragments (Myc), - gelified ligno-cellulosic fragments (GLC), pyrite.

Figure 2

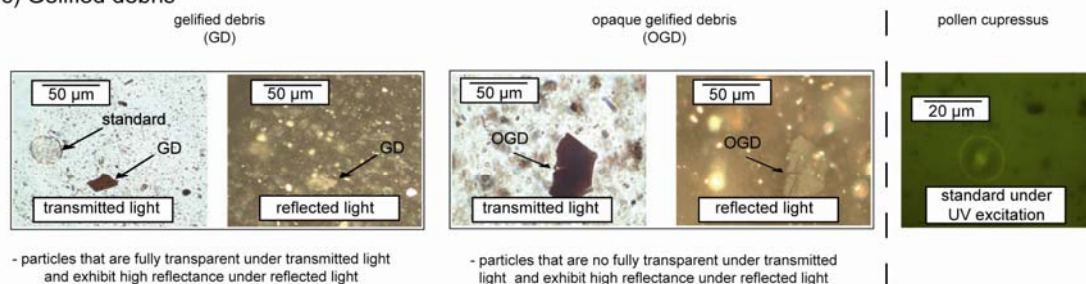
a) Amorphous particles



b) Ligno-cellulosic fragments



c) Gelified debris



d) Divers particles

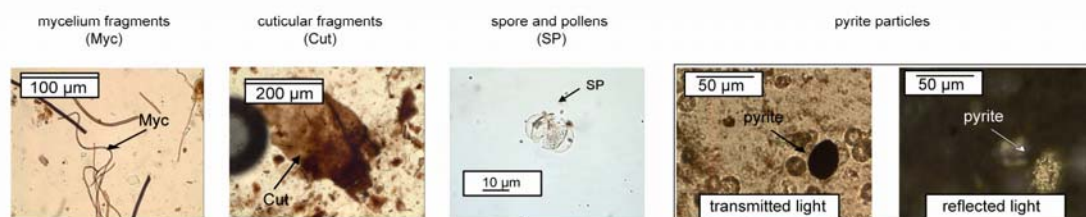


Fig. 3. Particles organic carbon amounts in different density fractions, a) humic layers sample (OH); b) compact fragment of rock sample (PL).

Figure 3

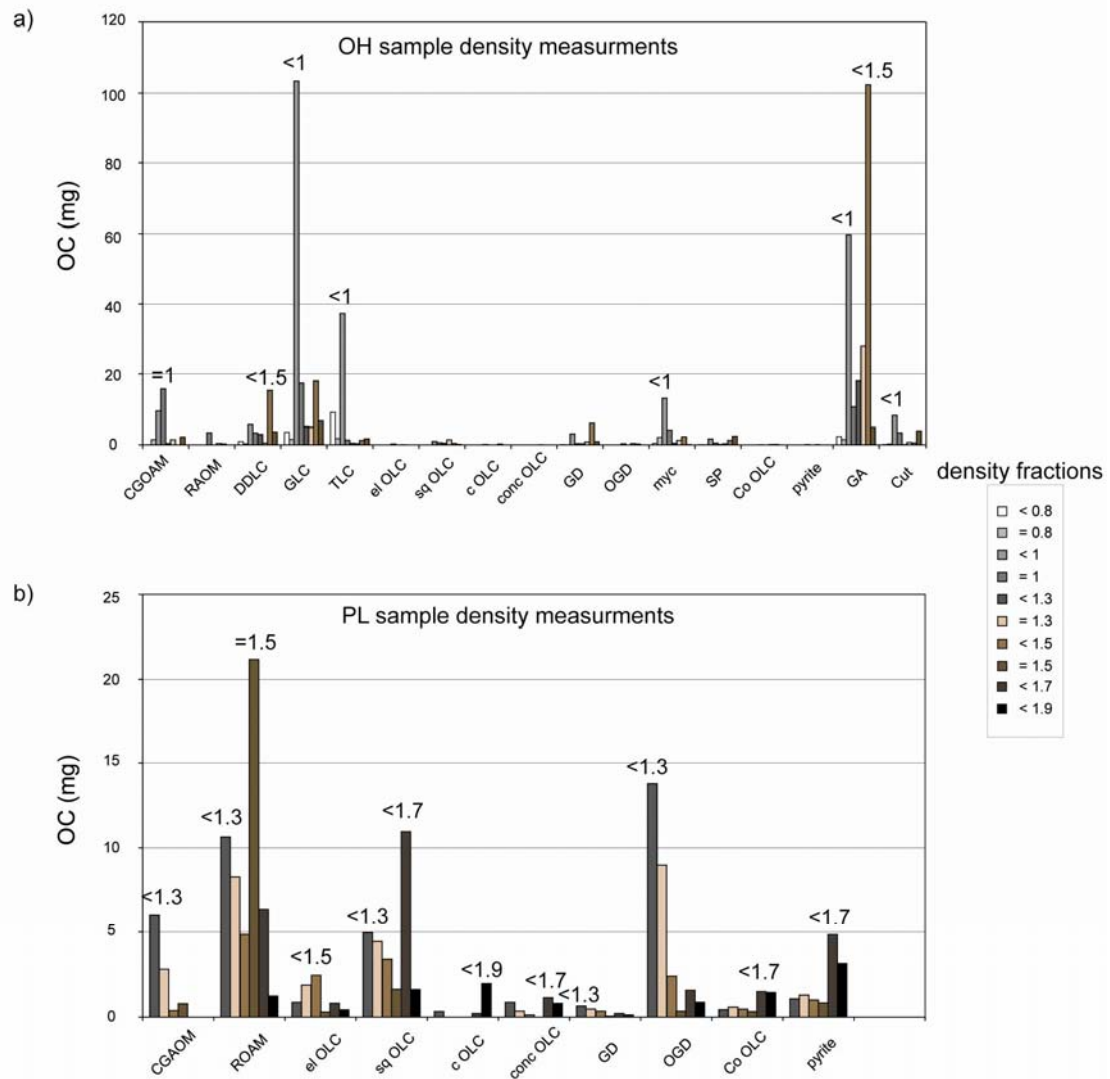


Fig. 4. P1 profile samples quantitative palynofacies counting. All opaque ligno-cellulosic are grouped as OLC; reddish amorphous organic matter (RAOM); all gelified debris are grouped as GDgr; all non opaque ligno-cellulosic fragments are grouped as LC; gelified amorphous organic matter (GA); mycelium, cuticular fragments and spore and pollens are grouped as divers (Div); clear and granular amorphous organic matter (CGAOM) and pyrite.

Figure 4

P1 profile

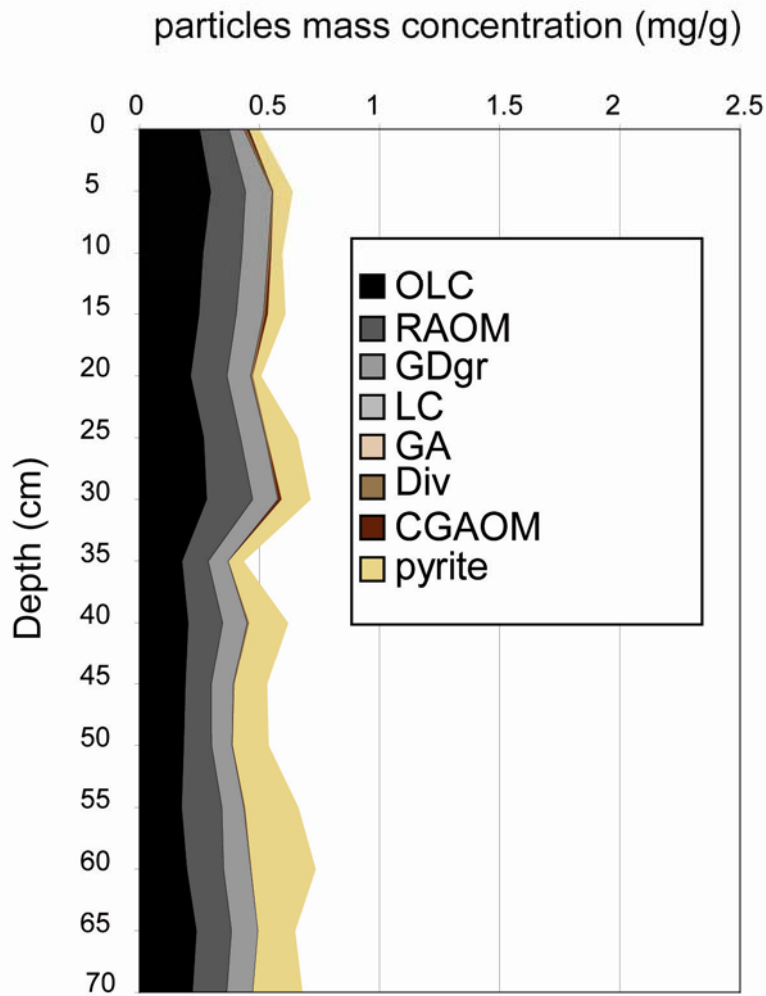


Fig. 5. Quantitative palynofacies counting ; a) P2 profile litter layer (OL) and humic layer (OH) samples; b) P2 profile organo-mineral layer (A) and compact fragments of rock samples (PL); c) P2 profile fine and friable elements samples (TF); d) P3 profile samples and e) riverine particle samples (suspended load samples - SL; bed load samples – BL). *All opaque ligno-cellulosic are grouped as OLC; reddish amorphous organic matter (RAOM); all gelified debris are grouped as GDgr; all non-opaque ligno-cellulosic fragments are grouped as LC; gelified amorphous organic matter (GA);*

mycelium, cuticular fragments and spore and pollens are grouped as divers (Div); clear and granular amorphous organic

Figure 5

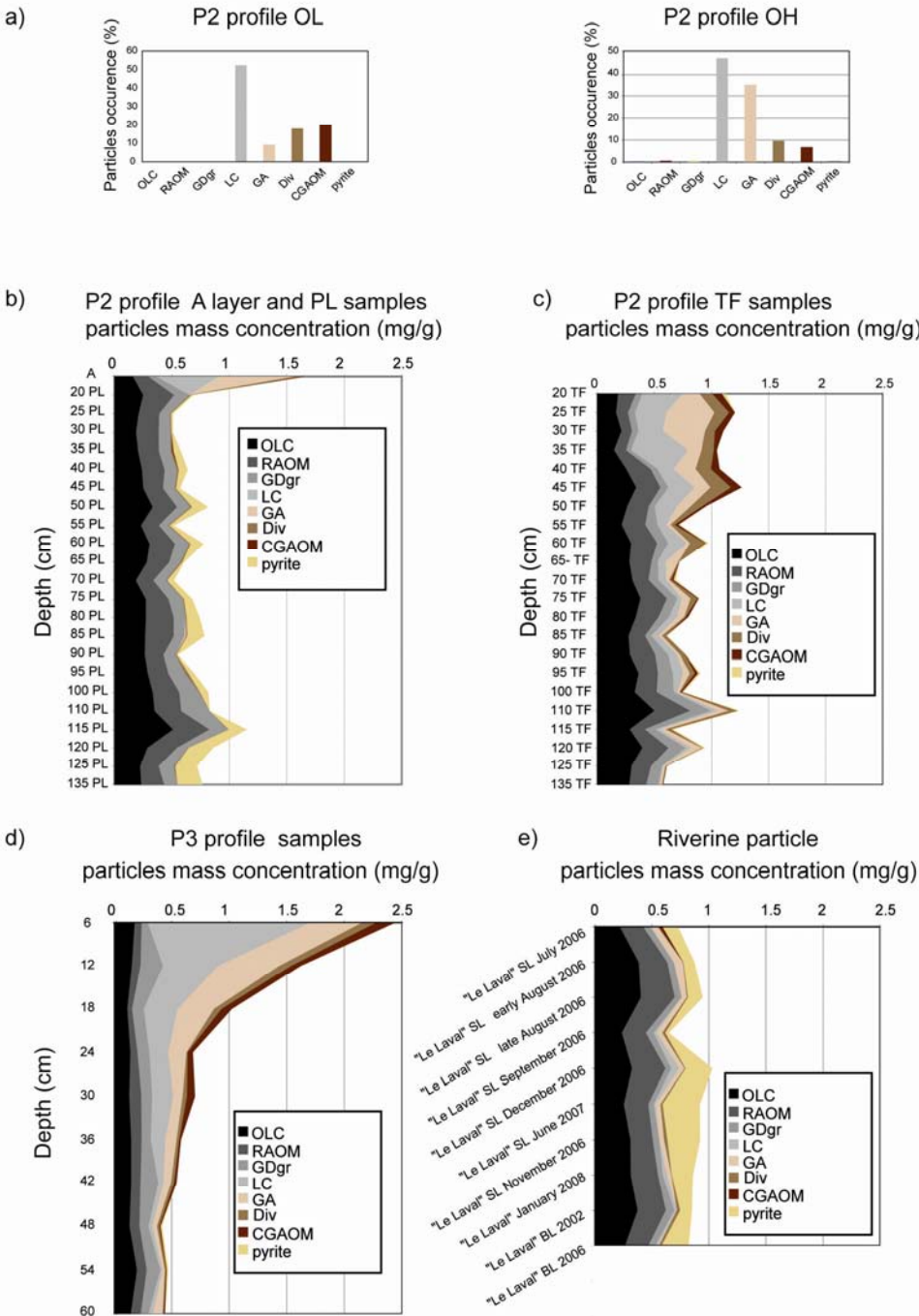


Fig. 6. Rock-Eval 6 measurements along P1 profile. *Total organic carbon (TOC - %); hydrogen index (HI - mg HC/ g⁻¹ TOC) and Tmax (°C).*

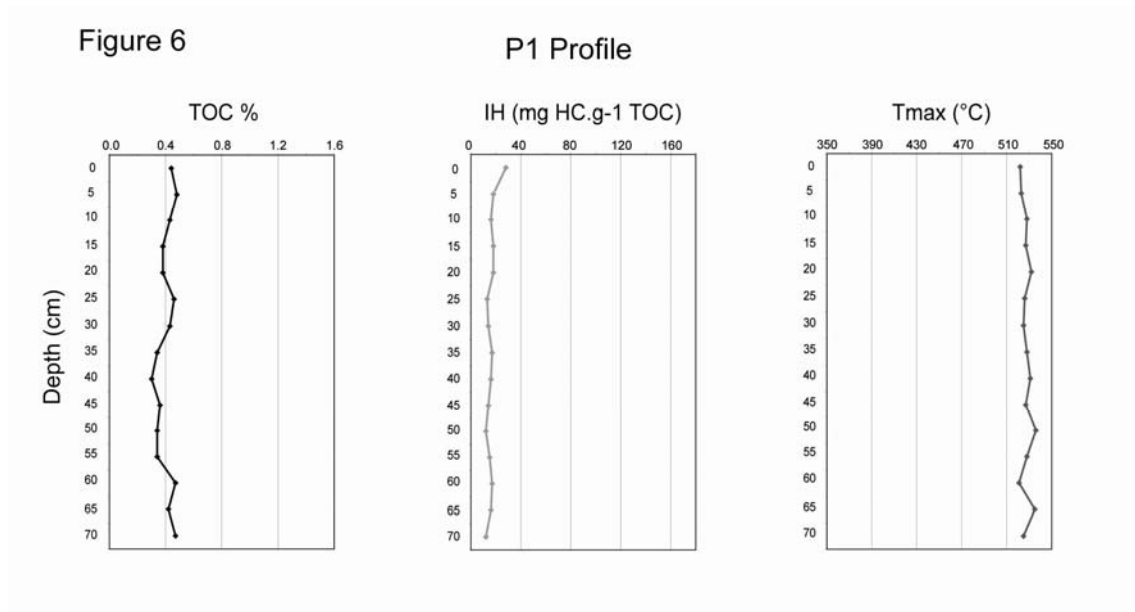
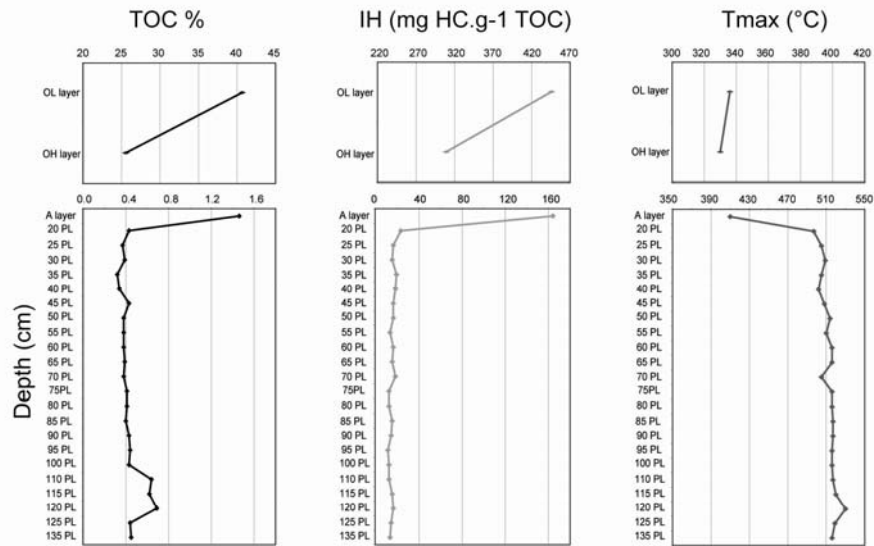


Fig. 7. Rock-Eval 6 measurements along (a) P2 profile compact fragments of rock samples (PL); (b) P2 profile fine and friable elements sample (TF); and (c) P3 profile samples. *Total organic carbon (TOC - %); hydrogen index (HI - mg HC/ g⁻¹ TOC) and Tmax (°C).*

Figure 7

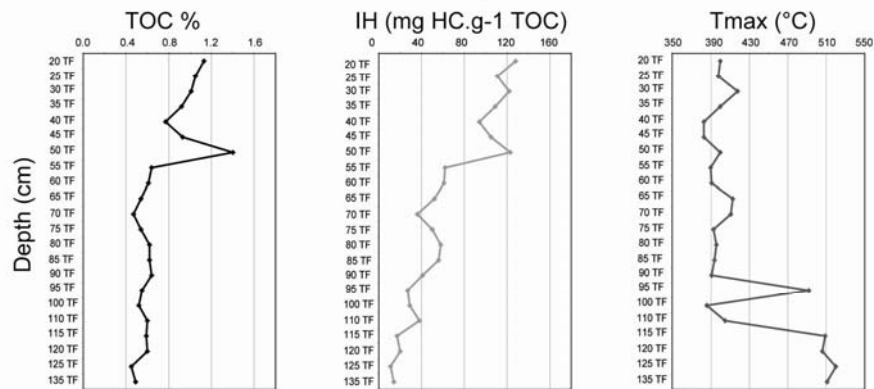
a)

P2 Profile
PL samples and soils layers



b)

P2 Profile
TF samples



c)

P3 Profile

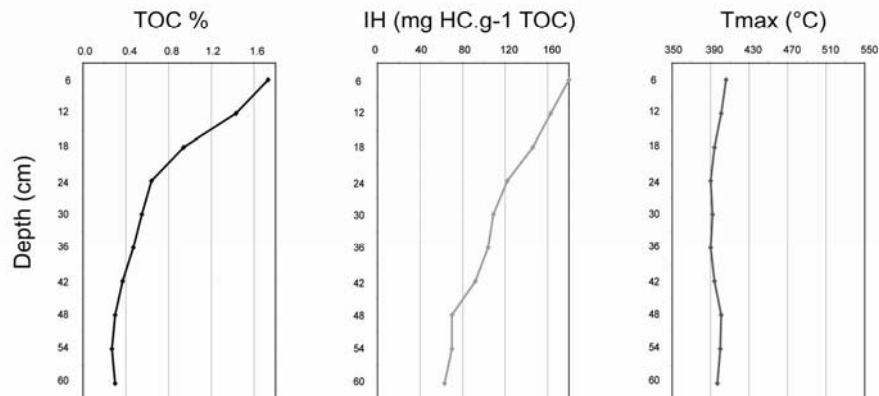


Fig. 8. Rock-Eval 6 measurements of riverine particles (suspended load – SL; and bed load samples - BL). *Total organic carbon (TOC - %); hydrogen index (HI - mg HC/ g⁻¹ TOC) and Tmax (°C).*

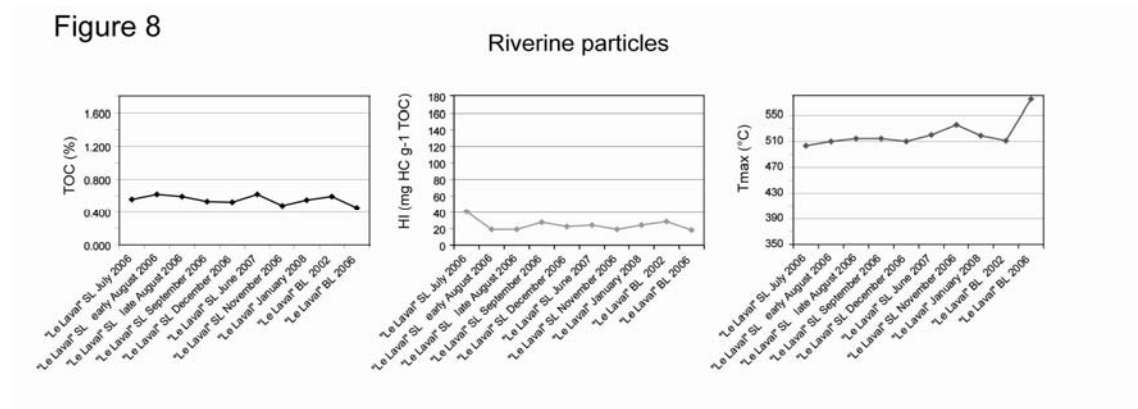


Fig. 9. Samples Al₂O₃ contents. *Compact fragments of rock samples (PL); organo-mineral layers sample (A); fine and friable elements samples (TF); suspended load samples (SL) and bed load samples (BL).*

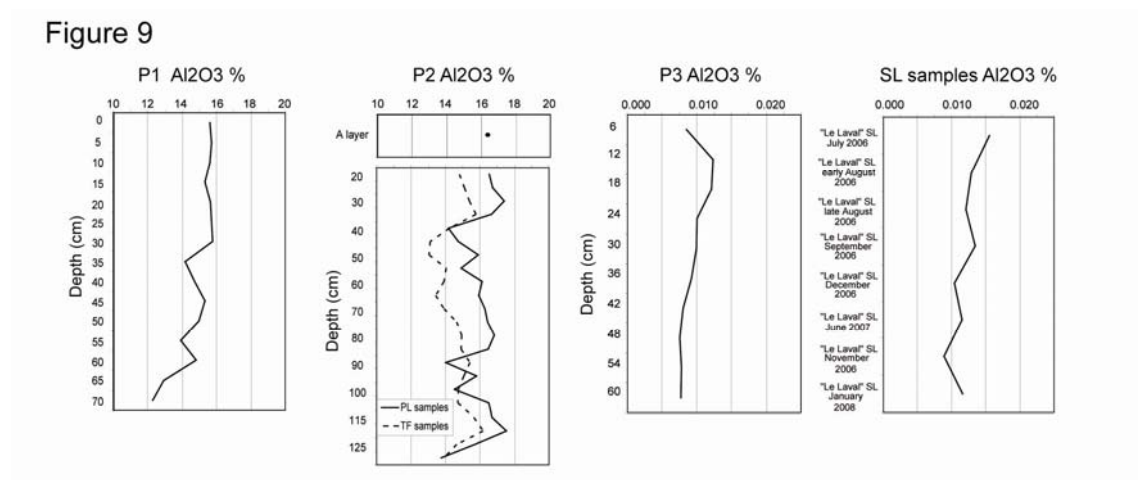


Fig. 10. Correlation between TOC (%) obtain by Rock Eval analysis and OC (wt%) calculated with quantitative palynofacies results.

Figure 10

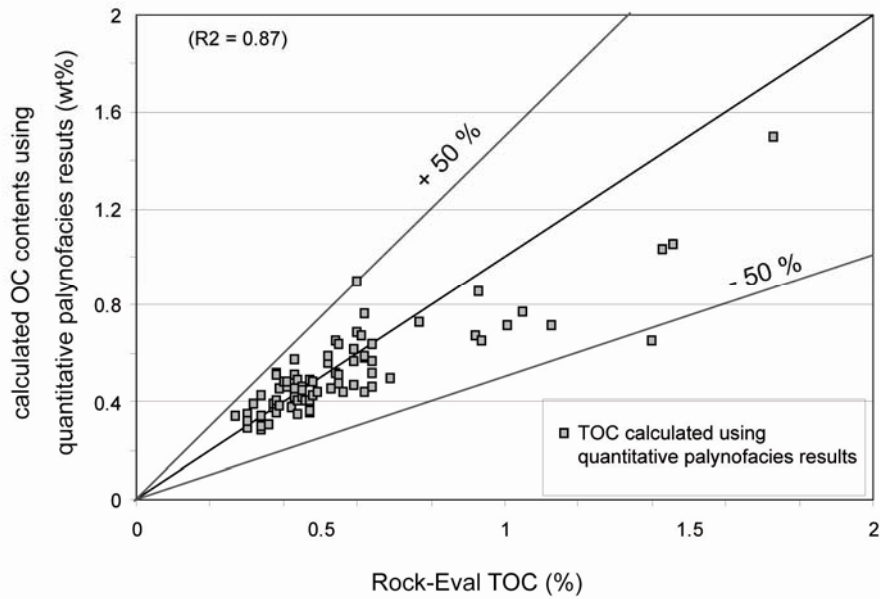


Fig. 11. Quantitative palynofacies results normalized against Al_2O_3 contents (noted AR) along profiles P1 (a); P2 (b); P3 (c) and riverine particles (d). FOM is the sum of OLC, ROAM and GDgr particles; ROM is the sum of LC, GA, CGAOM and Div. *Compact fragments of rock samples (PL); fine and friable elements samples (TF); suspended load samples (SL); bed load samples (BL); litter layers samples (OL); humic layers samples (OH) and organo-mineral layers samples (A).*

Figure 11

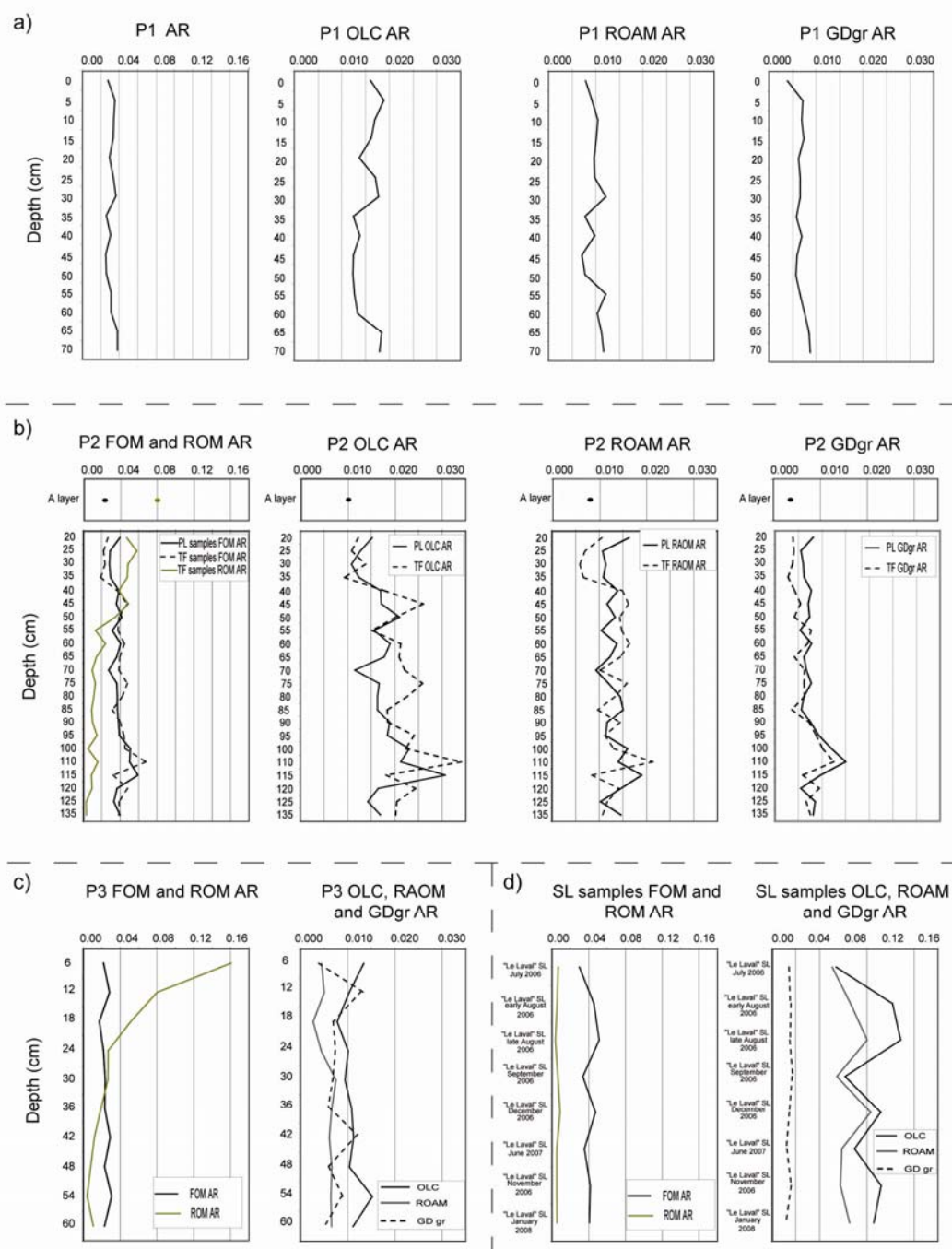


Fig. 12. Pyrite concentrations normalised against Al_2O_3 contents (noted AR) along studied profiles and riverine particles. *Compact fragments of rock samples (PL); fine and friable elements samples (TF); suspended load samples (SL); bed load samples*

(BL); litter layers samples (OL); humic layers samples (OH) and organo-mineral layers samples (A).

Figure 12

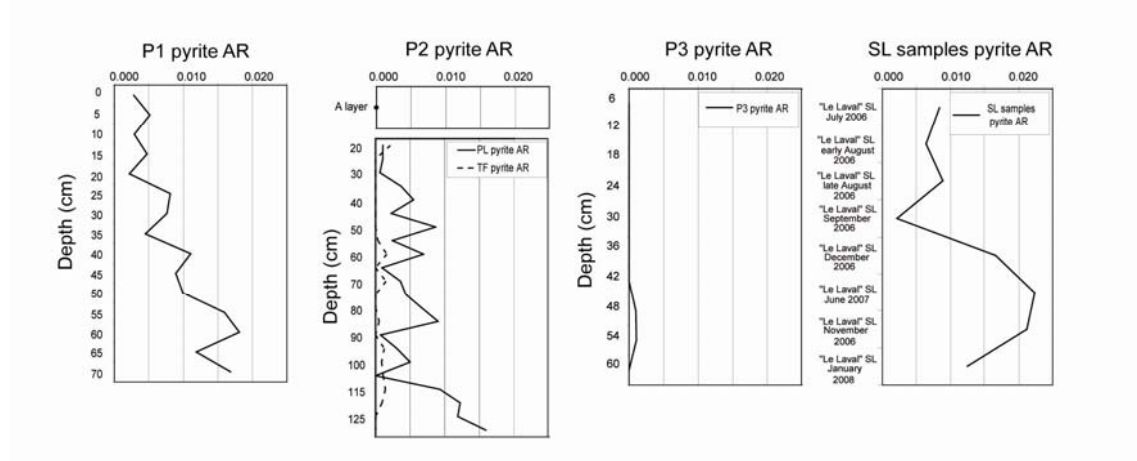


Table 1: Observed organic particles densities.

	CGAOM	RAOM	DDLC	GLC	TLC	el OLC	sq OLC	c OLC	conc OLC
Particles density	1	1.5	1.4	0.9	1.4	1.4	1.6	1.8	1.7
	GD	OGD	Myc	SP	Co OLC	pyrite	GA	Cut	Standard pollen
Particles density	1.2	1.2	0.9	0.9	1.7	5	1.4	0.9	1.3